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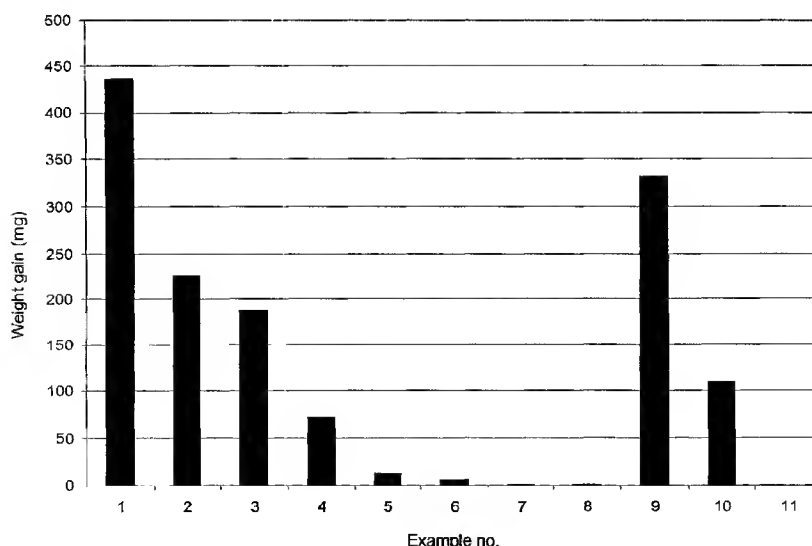
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(54) Title: COPPER BASED ALLOY RESISTANT AGAINST METAL DUSTING AND ITS USE



(57) Abstract: A copper-base alloy, which is resistant or immune to carburization, metal dusting and coking, resistant to oxidation and said alloy having the following composition (all contents in weight-%): Al > 0-15; Si ≥ 0-6; Mg ≥ 0-6, one or more of the group of Rare Earth Metal (REM). yttrium, hafnium, zirconium, lanthanum, cerium up to 0.3 weight-% each Cu balance and normally occurring alloying additions and impurities and use of said alloy as construction components in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes, for example, gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly, catalytic reforming under low-sulfur, and low-sulfur and low-water conditions and which is resistant to loss of material by copper vaporization.



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## COPPER BASED ALLOY RESISTANT AGAINST METAL DUSTING AND ITS USE

## FIELD OF THE INVENTION

5 The present invention relates to a Cu-base alloy, which is resistant or immune to carburization, metal dusting, coking and nitridation, and resistant to oxidation. The invention is also directed to the uses of said alloy in construction components in CO-containing atmospheres, and/or hydrocarbon-containing atmospheres or solid-carbon-containing processes or processes that contain  
10 ammonia and/or other reactive nitrogen-compounds as well as products formed from such alloys.

## BACKGROUND OF THE INVENTION

15 In the past, a number of inventions related to reforming processes in the petrochemical industry, have led to significant process efficiency improvements. One such example is the development of large pore zeolite catalysts, doped with specific metals, rendering the catalysts with a high selectivity which is suitable for precision-reforming and/or -synthesis, which for example has  
20 allowed more effective and economic production of a range of highly demanded commercial liquids based on hydrocarbon feedstocks. However, the catalysts were soon discovered to be sensitive to sulfur poisoning, leading to techniques to desulphurize the hydrocarbon feed being developed. Later, such catalysts were also found to be quickly deactivated by water, thus corresponding  
25 protecting technologies to lower the water content in the process gas streams were developed.

In turn, the low-sulfur and low-water conditions, led to the discovery of coke-formation and plugging within reactor systems; an effect which later was found to relate back to a severe form of disintegrating attack on metallic construction  
30 materials, which affects parts of the equipment such as furnace tubes, piping, reactor walls. This metal disintegrating mechanism was actually already known since the 1940's as "metal dusting", however, this phenomenon was seldom

seen because at the time reforming techniques included high sulfur levels in the process gas and very high reforming and synthesis pressures, since less effective catalysts were available.

Thus, with the above description of the historic developments as a background,  
5 it is understood that, in the petrochemical industry today there is a need for a solution against the effects of and the cause for metal dusting.

As earlier mentioned, metal dusting is a form of carburization where the metal disintegrates rapidly into coke and pure metal. The atomized metal particles, can be transported with the process gas, accumulates downstream on various  
10 reactor parts, and throughout the whole reactor system, metastasize catalytic coking that can create blockage.

It is generally appreciated that metal dusting is a large concern in the production of hydrogen and syngas ( $H_2/CO$  mixtures). In these plants, methane and various other higher hydrocarbons are reformed or partially oxidized to produce  
15 hydrogen and carbon monoxide in various amounts for use in producing other higher molecular-weight organic compounds. Increased reaction and heat-recovery efficiencies of the processes necessitate operating process equipment at conditions that favor metal dusting.

The need for increased heat recovery in ammonia-synthesis processes has  
20 caused metal dusting problems in the heat-recovery section of the reformed-gas system as well as in the reformer itself.

Metal dusting is also a problem in direct iron-ore reduction plants wherein reformed methane is dried and reheated to enhance ore-reduction efficiencies. Metal dusting occurs in the reformer, reformed-gas reheater and piping up-  
25 stream of the ore-reduction.

Metal dusting is also experienced in the heat-treating industry in equipment that handles items being treated (annealed, carburized).

Gases used in heat treating mix with oil residue on the items to form gases that are chemically favorable for metal dusting.

30 Gas mixtures used for carburizing can also cause metal dusting if control of chemistry of the process is not taken care of.

Petroleum refineries experience metal dusting in processes involving hydro-dealkylation and catalyst regeneration systems of "plat-former" units.

Other processes wherein metal dusting occurs are nuclear plants that employ carbon dioxide for cooling the equipment in the recycle-gas loop of coal-  
5 gasification units, in fired heaters handling hydrocarbons at elevated temperatures, iron-making blast furnaces in steel mills, and fuel cells using molten salts and hydrocarbons.

In recent years, there has been a strong emphasis on reforming and synthesis technology developments to make possible commercialization of remotely  
10 located, so-called "stranded gas reserves". The synthesis step, based on further developments of the Fischer-Tropsch process, will require the use of highly severe metal dusting causing compositions of the synthesis gas, with lower steam to carbon ratios and higher CO/CO<sub>2</sub> ratios, which will cause severe metal dusting. However, only small steps in the development in this direction have  
15 been taken due to lack of material with sufficient resistance to metal dusting.

#### DESCRIPTION OF THE RELATED ART

Other solutions used today, to provide protection against metal dusting and  
20 reduce coke formation, are the use of advanced nickel or iron base alloys with high amounts of chromium and certain additions of aluminum. Some surface modification methods based on diffusion techniques or coatings through overlay welding, laser-fusion, Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD) or spraying has also been tested. Many of these methods  
25 include materials based on transition metals, such as iron, nickel and cobalt, which are known for their catalytic properties that promote coke formation.

In environments comprising high contents of reactive nitrogen compounds, such as e.g. ammonia, metallic alloys can be affected of powerful nitridation,  
30 Examples of such environments are nitridation furnaces and annealing furnaces, which use a nitrogen-based atmosphere. Another example is power stations, which use the so-called Kalina-cycle. In those power stations a water-

ammonia mixture is used in order to transfer combustion heat from the furnace to the turbine in an analogue way as in steam boiler, but with a considerably improved efficiency. At those temperatures, which are in question for the ammonia-water mixture, 350°C-700°C, the gas mixture is highly intruding, and  
5 can cause extremely rapid corrosion courses on known alloys, such as steel of grade 304 (18 weight-% Cr, 9 weight-% Ni), iron-chromium-nickel-alloys of grade Alloy 800 (20 weight-% Cr, 31 weight-% Ni), nickel-alloy of grade Alloy 600 (16 weight-% Cr) and iron-chromium with 1-18 weight-% Cr. This is one factor that, which prevented the commercialization of Kalina-cycle power  
10 stations. Similar courses can also occur in the chemical process industry, which handles reactive nitrogen compounds, e.g. gaseous amines or amides. The solutions that are used nowadays in order to provide protection to metal dusting and reduce the formation of coke is the use of advances nickel- or iron-base alloys with high contents of chromium and certain additions of aluminium.  
15 Certain methods of surface modification, which are based on diffuion techniques or coatings by overlay welding, laser fusion, chemical vapor deposition (CVD), physical vapor deposition (PVD) or sputtering have been tested. Many of those methods include elements based on transition metals, such as iron, nickel and cobalt, which are known for their catalytic properties  
20 referencing to their promotion of the formation of coke.

There are metals, such as Cu and Sn, which are known to be resistant or immune to carburization and coke formation, but which have either a melting point, which is too low or insufficient oxidation resistance. The oxidation  
25 resistance is required in such cases where the solid coke is periodically removed by oxidation in steam and air. Consequently, the metal surfaces, which are in contact with the carburizing process gas, must also have adequate oxidation resistance, which in practice excludes Cu and low alloyed Cu as a useful carburization-resistant material. Even if the decoking step can be  
30 excluded in some processes, the start-up procedures after an inspection or other stops will be made easier by an alloy having certain oxidation-resistance. Further, breakdowns can lead to that the process gases will be contaminated

with e.g. sulfur, chlorine, alkali metallic compounds, water vapor and/or oxygen. A copper alloy, which is not protected of any oxide on the surface can thereby be affected of considerable corrosion. Likewise, copper alloys, which are protected by chromium oxide, can also be damaged of the above-mentioned compounds, because the oxidation resistance of the chromium oxide is limited. Finally, copper has, and in an even higher degree tin, high steam pressure at temperatures over 500°C, which results in that, when those elements are present on the surface of the metal, vapor of those can be transported into the process system and lead to contamination of e.g. construction material, process fluids and catalytics.

There are techniques existing to coat construction material with thin layers of resistant or immune metals or coking-resistant metals such as SN, Cu and are described in US-A-5,863,418 and EP-A-09003424. Such thin layers, <100µm thick, will thus be consumed by reaction with the construction material, for what reason the service time of such alloys is very short.

For the nitridation conditions, which occur in water-ammonia mixtures in Kalina-cycle power stations there nowadays does not exist any resistant material. For nitridation at higher temperatures, i.e. above 700°C, in most of the cases, a chromium oxide or silicon oxide or alumina forming iron-, cobalt or nickel-alloy often gets a temporarily protection of the formed oxide. Thus, also in those cases the service time of the material will be limited by nitridation.

## SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a copper-base alloy, which is resistant or immune to carburization, metal dusting, carburization and coking.

It is another object of the invention to provide a copper-base alloy resistant or immune to oxidation, especially resistant in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes, e.g. processes such as gasification of solid carbonaceous materials, thermal

decomposition of hydrocarbons and catalytic reforming, particularly, catalytic reforming under low-sulfur, and low-sulfur and low-water conditions.

It is another object of the invention to provide a copper-base alloy without the  
5 ability to catalytically activate the formation of solid coke.

It is a further object of the invention to provide a copper-base alloy which is resistant or immune to carburization, metal dusting and coking for use in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid  
10 carbon containing processes such as gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly catalytic reforming under low-sulfur, and low-sulfur and low-water conditions.

It is another object of the invention to provide a copper-base alloy resistant to  
15 loss of material by copper evaporation.

It is another object of the invention to provide a copper-base alloy resistant to nitridation in environments with reactive nitrogen, especially at temperatures between 300°C and 800°C, where conventional alloys strongly corrode.

Another object of the invention is to provide product forms in which this alloy  
20 can be used at temperatures where copper-base alloys themselves have too low strength.

#### BRIEF DESCRIPTION OF THE FIGURES

25 Fig. 1 shows diagrammatically the weight loss of some comparative samples and one example of the present invention after exposure at 650°C over a period of time of 1000 hours (4 cycles to RT) in  $25\text{CO}+3\text{H}_2\text{O}+\text{H}_2$ .

Fig. 2 shows a section in an phase diagram Cu-Ni-Al calculated with Thermo-calc for a given Al-content of 8%, where 1 – liquid, 2 – AlNi, 3 – FCC, 4 – BCC.

30 Fig. 3 shows the solubility of carbon (g carbon/g alloy) in an alloy with 4 weight-% Al and a varying Cu-Ni-relation at 750°C.



## DETAILED DESCRIPTION OF THE INVENTION

These objects are fulfilled with an alloy as described in the following.

## 5 Aluminum

Aluminum should be added for its capacity to form a protective alumina layer on the surface of the alloy in the temperature range of 300°C to 1300°C even in environments that solely contain trace of oxygen. Aluminium should be added in an amount up to 15 weight-%, preferably up to 13 weight-%, most preferably up to 8 weight-%, but not less than 2 weight-%, preferably not less than 4 weight-%.

## Silicon

Silicon can be used in order to promote the protective effect of aluminum in this type of alloy by forming aluminumsilicate, which has a higher formation rate compared to that of pure alumina. In this type of alloy the lower starting temperature for the formation of a protective oxide is favorable. Therefore silicon can be added to the alloy in order to improve the oxide formation at low temperatures. Thus, it is especially favorable for material which should be used in the temperature range of 300-900°C to alloy with silicon in a content of up to 6 weight-%, preferably up to 4 weight-%, most preferably between 1.5 weight-% and 4 weight-%. If the will be used at temperatures above 900°C, the content of silicon is positively for the oxidation resistance, but also an alloy which does not contain silicon, forms a protective alumina and therefor the content of silicon should be up to 6 weight-%, preferably 0-3 weight-%.

## Magnesium

Magnesia has the same properties as alumina in that it would reduce the oxidation rate of copper. Therefore, magnesium could to some extent replace aluminum in the alloy. The content of magnesium should therefore be limited to 0 – 6 weight-%, preferably up to 4 weight-%.

### Nickel, Iron, Cobalt

Transition metals, especially iron, nickel and cobalt, are known to have a strong catalytic effect on the formation of coke. The protecting capacity of the alumina layer, which will be formed on the surface of the alloy, however, makes that at proportionately high levels of these elements could be permitted, but not more than in a total of 60 weight-% of iron, nickel and cobalt.

Nickel can also be used in order to

- the maximum temperature of use by increasing the melting point of the alloy up to approximately 900°C and
- improve its mechanical strength at increased temperatures from approximately 800°C to approximately 1200°C.

Thus, an improved content of nickel can lead to an improved tendency to carburization and to a decreased resistance to metal dusting and coking. Therefore, the content of nickel should be kept as low as possible if the alloy should be used as coating on a load carrier for use in processes in the temperature range of 300°C to 800°C. Hence, if the alloy should be used without a load carrier at temperatures above 200°C or as coating on a load carrier at temperatures above 800°C it should be alloyed with nickel in an content not higher than 60 weight-%. In order to increase the mechanical strength and for applications at up to 900°C nickel in the alloy can completely or partly be replaced by iron and/or cobalt.

For use at higher temperatures, i.e. approximately 800°C to 1200°C nickel can be replaced by iron and/or cobalt in contents up to 25 weight-% of each element. Thus, in total at the maximum 40 weight-% of the nickel should be replaced.

A pure Cu-Al-alloy according to the present invention has a melting point between 1030°C and 1080°C, dependent on the content of Al. In order to be able to be used at temperatures above approximately 1000°C, especially above the above-mentioned melting point, it is necessary to alloy with e.g. nickel in order to increase the melting point of the alloy-system. For use above 1050°C the melting point at least be 1100°C and the alloy content of nickel 20-60 weight-%, preferably 25-45 weight-%.

If an optimum resistance to metal dusting and coking is desired, the content of one or more of the elements in this group of elements should be added in an amount not exceeding 2.0 weight-% per element. The total content of these elements should not exceed 6.0 weight-%, preferably not exceed 1.0 weight-%.

5

#### Reactive Additions

In order to further increase the oxidation resistance at higher temperatures, it is common practice to add a certain amount of reactive elements, such as Rare Earth Metals (REM), e.g. yttrium, hafnium, zirconium, lanthanum and/or cerium.

- 10 One or more of this group of elements should be added in an amount not exceeding 1.0 weight-% per element. The total content of those elements should not exceed 3.0 weight-%, preferably not exceed 0.5 weight-%.

#### Copper

- 15 The main component, which amounts the balance of the alloy of the present invention, is copper. Copper is known to be resistant or immune to catalytic activity and coking. Until today it has not been possible to use copper in these applications, due to its high oxidation rate when in contact with oxygen. The alloy comprises up to 98 weight-% Cu, but at least 38 weight-% Cu,  
20 preferably at least 73 weight-%, most preferably at least 80 weight-% Cu.

Further, the alloy comprises normally occurring alloying additions and impurities.

- 25 The alloy according to the present invention can be machined to construction material in the shape of tubes, pipes, plates, strip and wire or be used in the shape of coating on one or more surfaces of other commonly used construction materials in these shapes.

30

## DESCRIPTION OF PREFERRED EMBODIEMENTS OF THE INVENTION

## EXAMPLE 1

- 5 Statistical laboratory experiments were executed in a tube furnace in a strongly coking atmosphere. The metal dusting resistance of stainless steel of standard quality and the Cu-base alloys A to M of the present invention was measured and evaluated. Table 1 shows the chemical compositions of the investigated materials, Table 2 shows the compositions of the embodiments A to M
- 10 according to the present invention. All contents are given in weight-%.

Table 1

Example no.	C	Cr	Ni	Mo	N	Si	Mn	P	S	Ti	Ce
304L (bar)	0,013	18,35	10,15	0,39	0,043	0,42	1,26	0,024	0,004		
304L (plate)	0,015	18,20	10,10	0,39	0,043	0,43	1,42	0,021	0,001	-	-
Alloy 800HT	0,063	20,37	30,10	0,05	0,009	0,73	0,53	0,009	0,001	0,5	-
353MA	0,052	25,10	34,10	0,20	0,175	1,56	1,40	0,020	0,001	-	0,06

Table 2

	Al	Ni	Fe	Si	Mn	Cr	Mg	Bi	Ti	Zr	La	Cu
A	8,0	0,02	0,02		0,005	0,002		0,0001	0,0001	0,0001		balance
B	5,6	<0,1	<0,1	1,7	<0,1						0,0014	balance
C	9,5	<0,1	<0,1	4,8	<0,1						0,0012	balance
D	8,4	<0,1	<0,1	<0,1	<0,1						0,0004	balance
E	6,3	<0,1	<0,1	0,6	6,3						0,0007	balance
F	15,1	10,1	<0,1	<0,1	<0,1						0,0004	balance
G	2,8	<0,1	<0,1	0,1	<0,1						0,016	balance
H	4			6			6					balance
I	6			2								balance
J	8			2	8							balance
K	8				15		2					balance
L	12	8			8							balance
M	15	15										balance

15

The test samples were cut from plates or bars into a shape with dimensions of approximately 10 × 12 × 3 mm and prepared by grinding with 600 mesh. Some of the test samples were surface treated by a standard pickling operation

in 1.8M HNO<sub>3</sub> + 1.6M HF at 50°C during 8-40 min. or treated by an electro polishing operation (50g CrO<sub>3</sub> + 450ml orthophosphoric acid, 20V). The samples were cleaned in acetone prior to testing and placed in the cold furnace. In order to reach a low oxygen partial pressure, pure hydrogen was flushed through the furnace for three hours before introducing the reaction gas and heating to temperature. The gas flow rate was 250 ml/min, which corresponds to a gas velocity over the specimen of 9 mm/s. The temperature stabilizes at 650°C after 20 minutes heating. The input composition of the reaction gas was 25%CO+3%H<sub>2</sub>O +72%H<sub>2</sub>. The laboratory exposure was conducted at 650°C/1000h in a quartz tube furnace with a diameter of 25mm. Four temperature cycles down to 100-200°C and back to 650°C, each with a duration time of about 4-5h, were conducted in order to raise the carbon activity and promote initiation of metal dusting.

The results are presented as weight loss measurements after cleaning the samples from coke and graphite as presented in Figure 1, where:

Table 3. Description of the comparative examples

Example no.	Alloy	Product condition	Surface modification
1	304L	bar	annealed
2	304L	bar	electro-polished
3	304L	bar	ground
4	304L	bar	pickled
5	304L	plate	annealed
6	304L	cold rolled plate	ground
7	304L	cold rolled plate	electro-polished
8	800 HT	plate	ground
9	800 HT	plate	pickled
10	353 MA	plate	overpickled
11	Alloy A	plate	untreated

As shown in Figure 1, all comparative steels (Examples 1-10) suffered from metal dusting with formation of pits and coke during the 1000 h exposure as function of the measurable weight gain. However, the alloy of the present invention (Example 11) was practically non-reactive in this atmosphere with no weight change or coke formation. Example 11 has been exposed for totally

4000/hours in similar atmospheres (4x1000h at 650°C) with any measurable or visible changes.

Even if the present invention has been described by reference to the above-mentioned embodiments, certain modifications and variations will be evident to one of ordinary skill in the art.

The alloys according to the examples B to M with compositions according to Table 2 were produced by melting in a protective gas atmosphere of argon, followed by casting.

These alloys can, when exposed to oxidizing atmosphere in the temperature range of 300°to 1050°C, form a protective alumina or mixed aluminium containing oxide, which restrains further oxidation of the alloy and restrains evaporation of copper from the alloy, which makes the alloy more resistant to material loss by copper evaporation.

## EXAMPLE 2

The person skilled in the art realizes that the alloy according to the present invention could need a load carrier at elevated temperatures, i.e. temperatures above approximately 200°C. With this purpose the alloy of the present invention can be machined to a component in a composite or bimetallic composite solution, which will be used as construction material in the different shapes as mentioned above. The later is especially valid if the alloy has low contents of iron and nickel. In the compositions with high iron and/or nickel contents, the highest temperature, where the alloy can be used without any load carrier is considerably higher. For an alloy with 40 weight-% nickel, 5-15 weight-% aluminium and the balance copper, it could be estimated that the alloy has enough mechanical strength in order to be used up to 1000°C. Further, the mechanical properties of the alloy are strengthened by production of an alloy containing a continuous or discontinuous reinforcement with carbon fibers or silicon carbide fibers by a powder metallurgy. Further, such powder metallurgically produced alloy can also be reinforced by the presence of particle dispersions of oxides, e.g. alumina or nitrides. With these methods the temperature, where the alloy can be used without the presence of a load carrier,

can be extended to above 200°C. The alloy according to the present invention can be machined to construction material in the shape of tubes, pipes, plate, strip and wire.

- 5 If so required, the alloy can be produced in the shape of tubes or plate or strip, where the inner load-carrying layer is coated at one or both surfaces of the alloy according to the invention. Some of the methods, which can be used in order to produce a composite solution of the alloy and a load carrier are co-extrusion, co-welding or co-drawing and shrinkage of one tube on the load carrying
- 10 component and one outer and/or inner tube of the alloy according to the invention, possibly followed by a heat treatment in order to obtain a metallurgical binding between the components. A similar method at the production of plate or strip is to hot- or cold-roll together two or more plates or strips. Composite plates or –tubes can also be produced by explosion welding
- 15 of two or more different plates or tubes of a load carrier and the alloy according to the invention. An outer- and/or inner-component can also be applied on a load carrier by help of a powder metallurgical technique, such as HIP (Hot Isostatic Pressing) or CIP (Cold Isostatic Pressing). In these cases the load carrier could be in the shape of tubes, pipes, plate, strip or wire or other suitable
- 20 product form. After pressing, the formed composite will be further machined by e.g. hot extrusion and/or welding, drawing and forging.

- Other methods for the production for the production of composite material are electrolytic coating of copper and aluminium on the load carrying component,
- 25 possibly followed by an annealing in order to homogenize the coating or a gas phase deposition of copper and aluminium by e.g. vaporization, pack cementation, sputtering, chemical vapor deposition (CVD) or other methods. Aluminium and copper can also be deposited on the load carrier e.g. by dipping in a melt or by overlay welding. These methods are possible to use in order to
- 30 produce all of the above-mentioned product forms. Different coating methods can be used in order to supply copper and aluminium to the alloy. In such

cases, a final heat-treatment is required in order to homogenize the alloy with the purpose to keep its corrosion properties.

Composite strip or composite plates, produced according to the above description can be welded together to longitudinal welded or helical welded  
5 composite tubes with the alloy according to the invention on the inner and/or outside of the tube.

Suitable load carriers in the above mentioned product forms are such high temperature alloys, which today are used in the actual temperature range. This  
10 concerns for temperatures lower than 700°C martensitic or bainitic or ferritic iron alloys with additions of e.g. chromium, molybdenum, vanadium, niobium, tungsten, carbon and/or nitrogen in order to obtain mechanical strength at high temperature. At temperatures above approximately 500°C it is usual to use austenitic iron-chromium-nickel alloys, which are possibly mechanically  
15 strengthened as load carrier by alloying with e.g. molybdenum, vanadium, niobium, tungsten, carbon and/or nitrogen. In both of those groups of alloys chromium and sometimes aluminium and/or silicon is used in order to give the load carrier an improved corrosion resistance. In those cases, where the alloy according to the invention is deposited on both surfaces of such load carrier, the  
20 alloy according to the invention will deliver the corrosion resistance that is required. But that means, alloys whose maximum temperature of use in other applications is limited by the corrosion resistance being able to be used as load carriers at higher temperatures than otherwise. In those cases, where the alloy according to the invention is only deposited at one surface of the load carrier, it  
25 is necessary that the load carrier itself has a sufficient corrosion resistance in the environment its free surface is exposed for.

### EXAMPLE 3

Fig. 2 shows a section of a phase diagram Cu-Ni-Al calculated with Thermo-  
30 calc for a given Al-content of 8%. Graph 1 shows the solidus/liquidus temperature, graph 2 shows the area of stability for the phase NiAl, graph 3 shows the area of stability for the cubic close-packed solid solution of copper



and nickel, which also can contain minor contents of e.g. aluminium. Graph 4 shows the area of stability for the phase, which in the pure Cu-Al-system is called  $\beta$ .

Figure 2 shows the effect of different contents of copper and nickel in an alloy of 92 weight-% (Cu+Ni) and 8 weight-% Al at the solidus- and liquidus temperatures. This figure shows that by increasing the content of nickel above 20 weight-% its melting point can be brought to exceed 1000°C. By that means it could be calculated, that the maximum temperature of use for the alloy according to the invention is 1200°C.

Figure 3 shows the effect of the nickel content of an alloy on the solubility of the carbon in it. This diagram shows for nickel contents above approximately 10 weight-% the solubility of carbon is strongly improved together with increasing nickel content. The rate of carburization of an alloy is to a highly extent determined by the solubility of carbon in the alloy and also the phenomena of metal dusting and coking are expected to increase with increasing carbon solubility. Therefore, it is desirable that the solubility of carbon in the alloy is as low as possible, and a consequence of this is that the nickel content should be lower than 10 weight-% in order to obtain an optimum resistance to carburization, coking and metal dusting, preferably lower than 1 weight-%.

The reason for such low level of the Ni-content is required in order to obtain optimum properties is, that nickel, besides that it affects the solubility of carbon also catalyzes coking, which is unfavorable.

Table 3

Example	Ni weight-%	Al weight-%	Cu weight-%	Solidus temperature °C	Carbon solubility at 750°C g carbon/g alloy
	0	4	96	1070	2,50E-13
	2	4	92	1080	3,30E-13
	5	4	91	1090	3,50E-13
	10	4	86	1100	6,60E-13
	20	4	76	1130	5,00E-12
	30	4	66	1160	7,00E-11
	40	4	56	1190	1,20E-09
	50	4	46	1230	1,90E-08
	0	8	92	1040	9,65E-13

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	2	8	90	1030	8,22E-13
	5	8	87	1040	5,40E-13
	10	8	82	1070	3,00E-13
	20	8	72	1100	8,00E-13
	30	8	62	1130	7,00E-12
	40	8	52	1150	1,00E-10
	50	8	42	1180	2,40E-09
Comp. example	60	4	36	1270	1,90E-07
Comp. example	60	8	32	1200	7,00E-08

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## Claims

1. Copper-base alloy, **characterized** in that said alloy is resistant or immune to carburization, metal dusting and coking and resistant to oxidation and has the following composition (all contents in weight-%):
- Al        >0 - 15  
Si        ≥0 - 6  
Mg        ≥0 - 6
- One or more of the group of Rare Earth Metals (REM),  
such as Yttrium, Hafnium, Zirconium, Lanthanum, Cerium  
up to 1.0 weight-% of each element  
Cu        balance  
and normally occurring alloying additions and impurities.
2. Copper-base alloy according to claim 1, **characterized** in that said alloy comprises up to 15 weight-% Al, preferably up to 13 weight-% Al, most preferably up to 8 weight-% Al, but at least 2 weight-% Al and the balance Cu and normally occurring alloying additions and impurities.
3. Copper-base alloy according to claim 1 and 2, **characterized** in that said alloy comprises up to 6 weight-% Si, preferably up to 5 weight-% Si and the balance Cu and normally occurring alloying additions and impurities.
4. Copper-base alloy according to any of the preceding claims, **characterized** in that said alloy comprises up to 6 weight-% Mg, preferably up to 4 weight-% Mg and the balance Cu and normally occurring alloying additions and impurities.
5. Copper-base alloy according to any of the preceding claims, **characterized** in that said alloy comprises one or more of the group of Rare Earth

Metal (REM), Yttrium, Hafnium, Zirconium, Lanthanum, Cerium in a content up to 0.3 weight-% each.

6. Copper-base alloy according to any of the preceding claims, **characterized** in that said alloy is resistant to oxidation in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes, for example, gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly, catalytic reforming under low-sulfur, and Low-sulfur and low-water conditions.
7. Use of a copper-base alloy according to any of the preceding claims as construction material in the shape of tubes, pipes, plate, strip and wire.
8. Use of a copper-base alloy according to any of the preceding claims as one component in a composite material in the shape of tubes, pipes, plate, strip and wire in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes, for example, gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly, catalytic reforming under low-sulfur, and low-sulfur and low-water conditions.
9. Use of a copper-base alloy according to any of the preceding claims as one component in a composite material.
10. Use of a copper-base alloy according to claim 6, where the copper-base alloy as one component in a composite material.
11. Use of a copper-base alloy containing (in weight-%):
- |    |          |
|----|----------|
| Al | up to 20 |
| Si | ≥0 - 6   |
| Mg | ≥0 - 6   |

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One or more of the group of Rare Earth Metals (REM),  
such as Yttrium, Hafnium, Zirconium, Lanthanum, Cerium

up to 1.0 weight-% of each element

One or more of the elements iron, nickel, cobalt,

5 In total up to 60 weight-%.

Cu balance

and normally occurring alloying additions and impurities.

in CO-containing atmospheres, and/or hydrocarbon containing atmospheres

or solid carbon containing processes, for example, gasification of solid

10 carbonaceous materials, thermal decomposition of hydrocarbons and  
catalytic reforming, particularly, catalytic reforming under low-sulfur, and  
low-sulfur and low-water conditions.

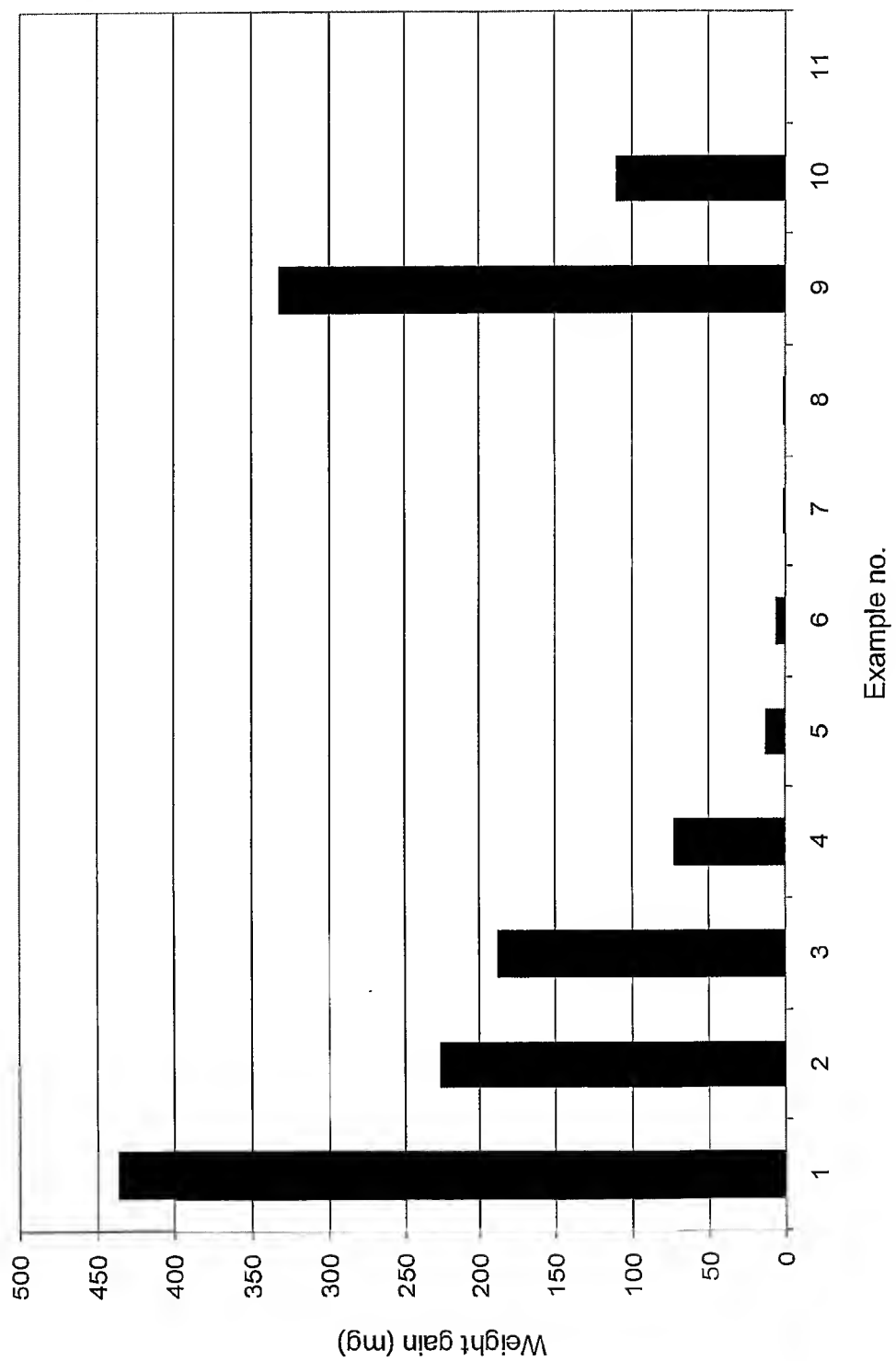
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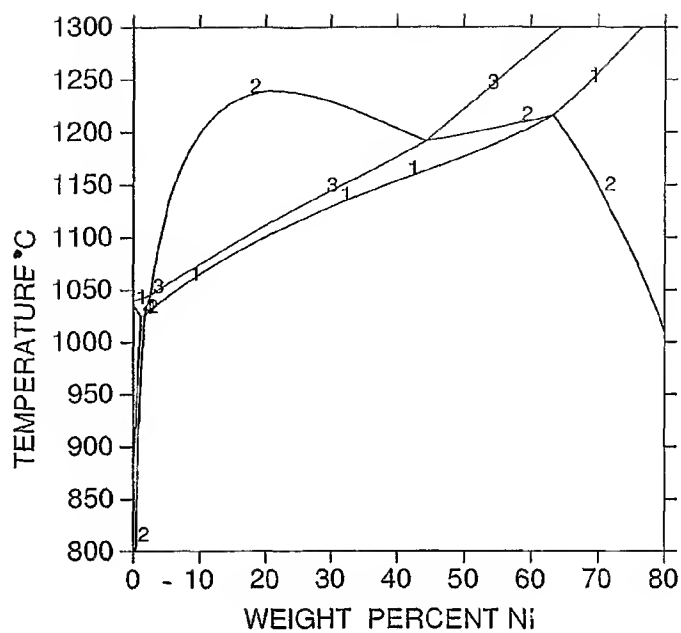
1 / 2

Figure 1

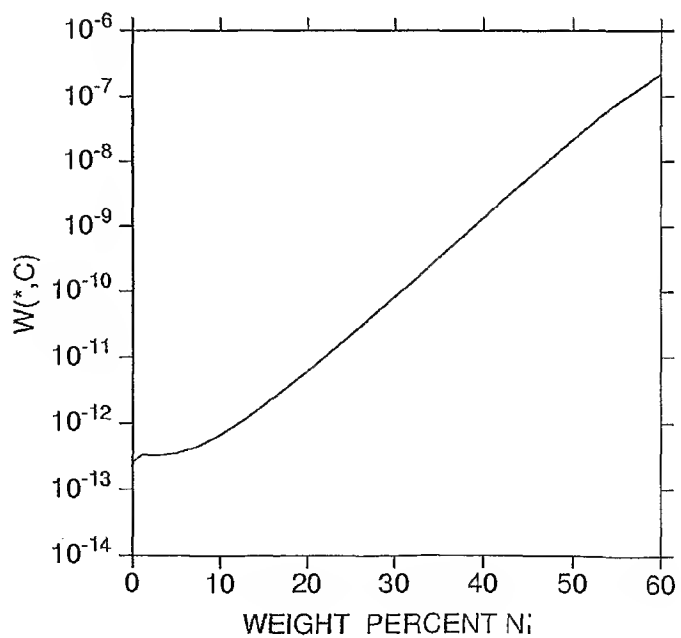


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Figur 2



Figur 3



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB 03/01567

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22C 9/01

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL

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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

23 June 2003

Date of mailing of the international search report

24-06-2003

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB 03/01567

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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International application No.

PCT/IB 03/01567

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